



Laser-Induced Breakdown Spectroscopy: Capabilities and Applications

by Jennifer L. Gottfried and Frank C. De Lucia, Jr.

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Laser-Induced Breakdown Spectroscopy: Capabilities and Applications

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14. ABSTRACT This work provides a review of the capabilities and applications of laser-induced breakdown spectroscopy (LIBS) at the U.S. Army Research Laboratory (ARL). By coupling advances in LIBS hardware and analysis software, ARL has expanded the capabilities of LIBS significantly. LIBS uses a focused, pulsed laser to ablate a target material, generating a transient microplasma which emits light characteristic of the sample composition. It is a real-time sensor technology which requires no sample preparation and provides universal materials detection for solids, liquids, and aerosols. Applications investigated at ARL in recent years include the standoff detection of explosive residues and other hazardous materials, plastic landmine discrimination, and material characterization of various metal alloys and polymers.					
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1. Introduction to LIBS

Laser-induced breakdown spectroscopy (LIBS) is a spectroscopic analysis technique that uses the light emitted from a laser-generated microplasma to determine the composition of a sample based on elemental and molecular emission intensities (I). The ability of LIBS to provide rapid, multi-element microanalysis of bulk and residue samples (solid, liquid, gas, and aerosol) in the parts-per-million range with little or no sample preparation has been widely demonstrated (2–9) and is the greatest advantage of LIBS compared with other analytical approaches. Field-portable LIBS instruments have been demonstrated for many applications, including the determination of lead (Pb) in soil and paint (10), the online sorting of wood (11), and the analysis of paints and coatings (12). Standoff LIBS instruments have been demonstrated at distances >100 m for environmental (13) industrial (14, 15), cultural heritage (16), and geological (17, 18) applications. Figure 1 shows a diagram of a simple LIBS system and lists several key advantages.

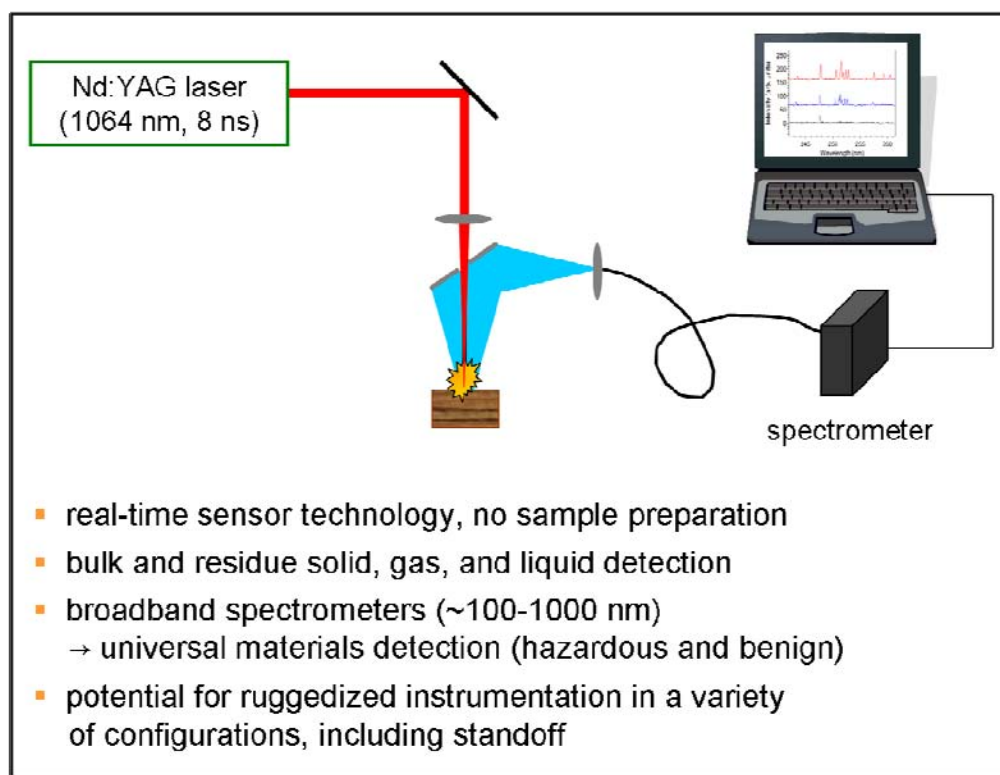


Figure 1. Diagram of a typical LIBS system. The laser ($\sim\text{GW}/\text{cm}^2$) is focused onto the sample surface with a lens, resulting in the ablation of a small amount of material and the subsequent formation of microplasma above the sample surface. The light emitted from the plasma is collected and focused onto a fiber optic attached to a spectrometer, which spectrally and temporally resolves the light. A PC displays and analyzes the recorded spectra, which are characteristic of the target material.

LIBS has the following properties: (1) it requires no sample preparation; (2) is sensitive enough that only nanograms–picograms of material is required for production of a usable LIBS spectrum; (3) provides real-time (<1 s) response; (4) LIBS sensors can be made rugged and field-portable; (5) all components (i.e., laser, detector, computer, etc.) can be miniaturized; and (6) LIBS offers the flexibility of point detection or standoff mode operation. LIBS used in conjunction with broadband detectors (ultraviolet [UV]-visible[VIS]-near-infrared[NIR] spectral range) can determine the elemental composition of any target material since every element on the periodic table has characteristic atomic emission lines in the UV-VIS-NIR spectral range. Although most early LIBS applications involved metal targets, LIBS has recently been applied to a variety of materials including plastics and other organic compounds, biological materials, and hazardous substances. No other sensor is capable of real-time detection of all classes of chemical compounds in all states of matter with no sample preparation.

2. Background/Expertise

Researchers at the U.S. Army Research Laboratory (ARL) in the Weapons and Materials Research Directorate (WMRD) have been developing LIBS for a variety of applications since the early 1990s. ARL has used LIBS for the detection of Halon alternative agents (19, 20), tested a field-portable LIBS system for the detection of lead in soil and paint (10), studied the spectral emission of aluminum and aluminum oxide from bulk aluminum in different bath gases (21), performed kinetic modeling of LIBS plumes (22–25), and demonstrated the detection and discrimination of geological materials (18, 26–31), plastic landmines (32, 33), explosives (34–42), and chemical and biological warfare agent surrogates (43–47). ARL has also published a number of reviews on LIBS (8, 48–52). Figure 2 shows photographs of several ARL LIBS systems: (a) a laboratory LIBS setup, (b) a commercial LIBS system by Ocean Optics, Inc., (c) a prototype man-portable LIBS device, and (d) a prototype standoff LIBS system developed for 100+ m detection and discrimination of explosive residues.

3. Example Applications

3.1 Identification of Materials

The identification of metals is the most straightforward application of LIBS, since most metals have strong atomic emission intensities in the ultraviolet and visible regions. Figure 3 shows the broadband LIBS spectra of several high purity metal foils, demonstrating distinct differences in the emission spectra. The spectra were recorded with a double-pulse laser system (two 420 mJ laser pulses at 1064 nm separated by 2 μ s) with an argon gas flow. Most of the emission lines above 700 nm are due to the argon.

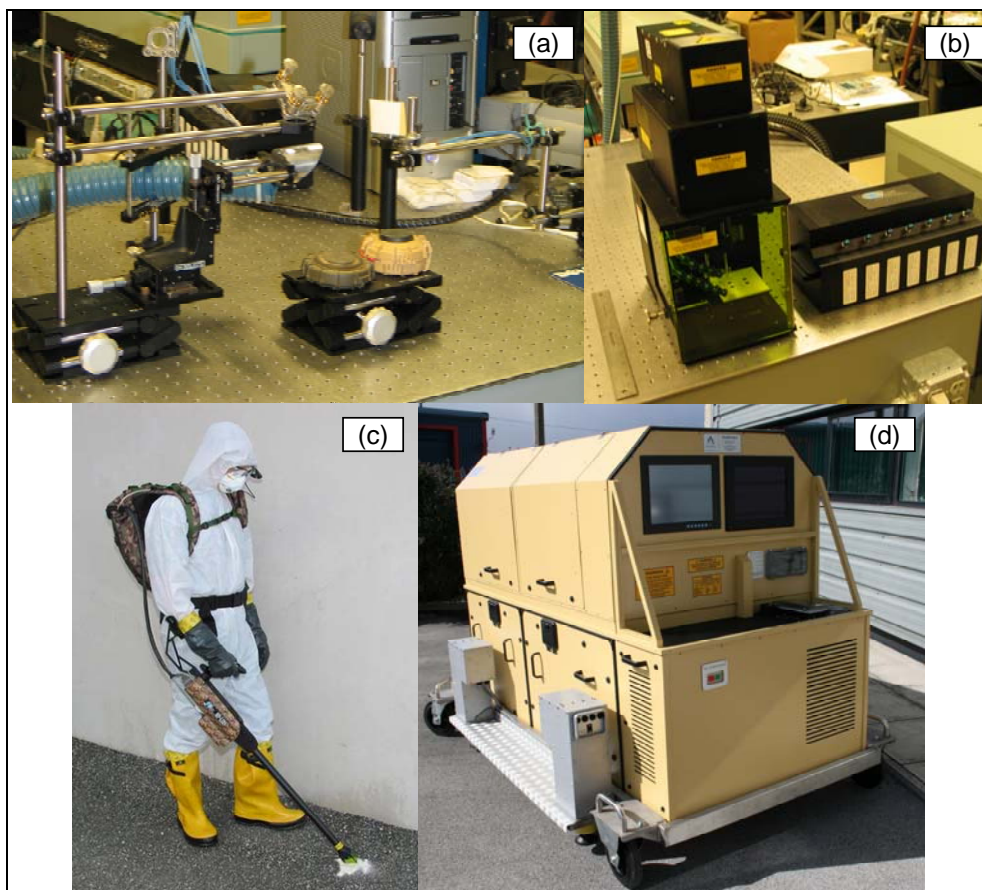


Figure 2. Photographs of ARL LIBS systems: (a) a laboratory LIBS setup, (b) a commercial LIBS system by Ocean Optics, Inc., (c) a prototype man-portable LIBS device, and (d) a prototype standoff LIBS system developed for 100+ m detection and discrimination of explosive residues.

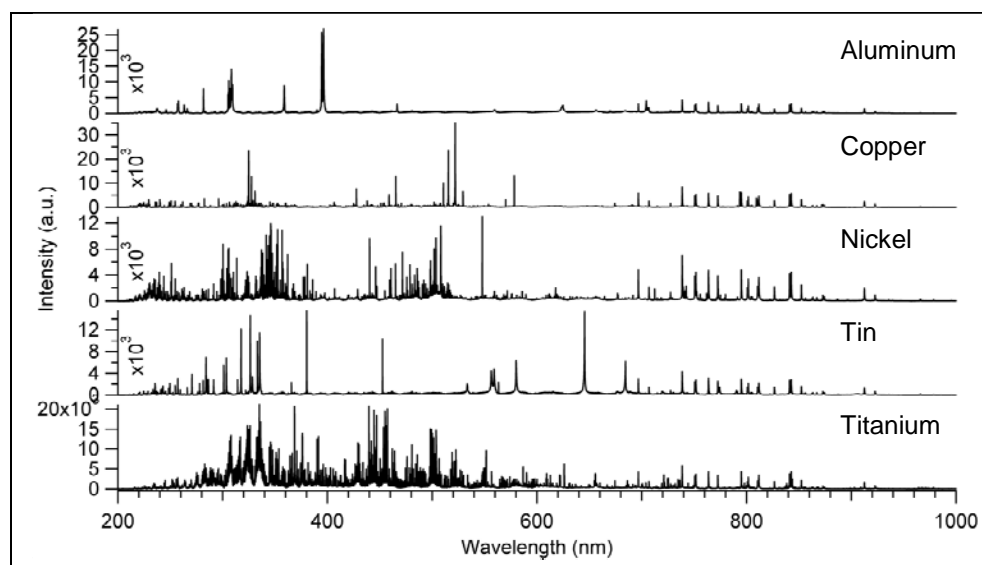


Figure 3. Double-pulse LIBS spectra of aluminum (99.999%), copper (99.999%), nickel (99.98%), tin (99.998%), and Ti (99.998%) under an argon bath gas.

With recent advances in broadband spectrometers and chemometric analysis techniques, the identification of non-metals has become increasingly widespread with LIBS. LIBS has been used for the identification of polymers (43–57), thermoplasts (58–60), and other organic compounds (61, 62), including explosives (34–42, 63–65). Figure 4 shows the LIBS spectra of various thermoplastic polymers from McMaster-Carr acquired with a commercial LIBS system (Applied Photonics, Ltd). Strong emission lines from carbon (C), hydrogen (H), nitrogen (N), oxygen (O), cyanogen (CN), and diatomic carbon (C_2) are present in the spectra.

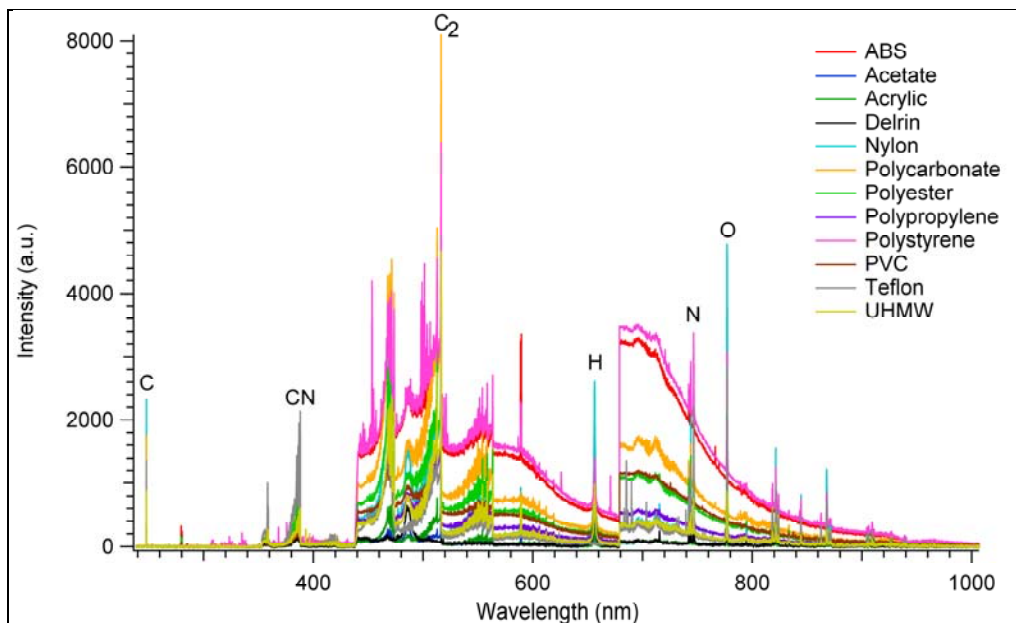


Figure 4. Single-pulse LIBS spectra of various thermoplastics from McMaster-Carr acquired on a commercial LIBS system (Applied Photonics, Ltd.).

3.2 Material Characterization

Another important application for LIBS is material characterization, i.e., trace impurity identification. The ability of LIBS to detect trace impurities in different aluminum alloys is demonstrated in figure 5. Observed impurity emission lines include beryllium (Be), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), silicon (Si), tin (Sn), strontium (Sr), titanium (Ti), and zinc (Zn). Table 1 lists the certified impurity concentrations for each NIST alloy; the red text indicates that no emission lines were observed in the LIBS spectra for the specified element and alloy.

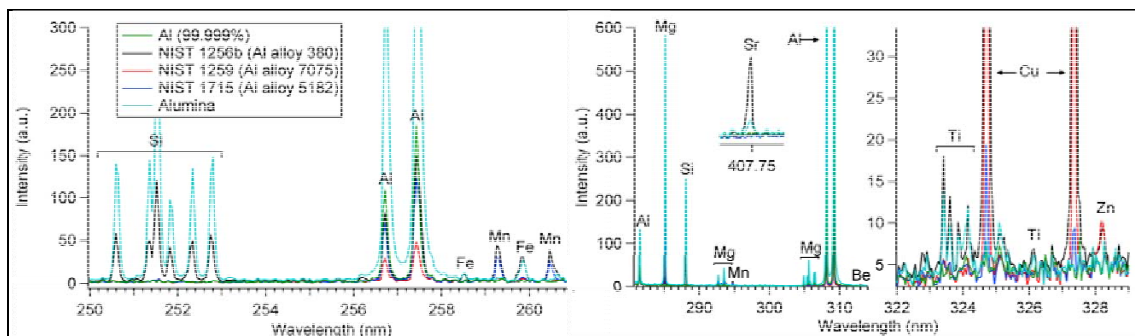


Figure 5. Single-pulse LIBS spectra of pure aluminum, three NIST-certified standard alloys, and alumina (Al_2O_3). Observed trace impurities include Be, Cu, Fe, Mg, Mn, Ni, Si, Sn, Sr, Ti, and Zn.

Table 1. NIST-certified standard concentrations of impurities in aluminum alloys by percent weight (red text indicates emission lines for that element were not observed).

	Be (%)	Cr (%)	Cu (%)	Fe (%)	Mg (%)	Mn (%)	Ni (%)	Pb (%)	Si (%)	Sn (%)	Sr (%)	Ti (%)	V (%)	Zn (%)
Al 1256b	—	0.0572	3.478	0.865	0.0637	0.3857	0.4135	0.1075	9.362	0.35	0.0188	0.877	0.0212	1.011
AL 1259	0.025	0.173	1.60	0.205	2.48	0.079	0.063	—	0.18	—	—	—	—	5.44
AL 1715	—	0.034	0.0494	0.199	4.474	0.3753	0.0195	0.015	0.1553	—	0.0002	0.0335	0.0174	0.0505

LIBS has also been used for the characterization of solder materials. Increasing environmental concerns have led to the introduction of “green” replacements for lead-containing solder materials. Unlike older solder materials that consist primarily of lead, these “lead-free” solders are predominantly tin that has been alloyed with small amounts of copper or silver. Because high-content tin materials have been shown to develop tin “whiskers” (tin nanowire structures) that can cause catastrophic electrical shorts in electrical circuit boards, the military has not yet adapted the “lead-free” standard. Furthermore, mixing of lead and “lead-free” solders may result in brittle and cracked joints prone to premature failure. The continued reliability of many fielded military devices depends on ensuring that repairs are performed using compatible solder materials. In an initial “proof of principle” study, we investigated the potential of LIBS for characterizing solder compositions (66). Figure 6 shows LIBS spectra comparing a Pb-containing solder and a Pb-free solder. As shown in table 2, 100% of the test spectra from seven solder types were correctly identified as Pb-containing or Pb-free.

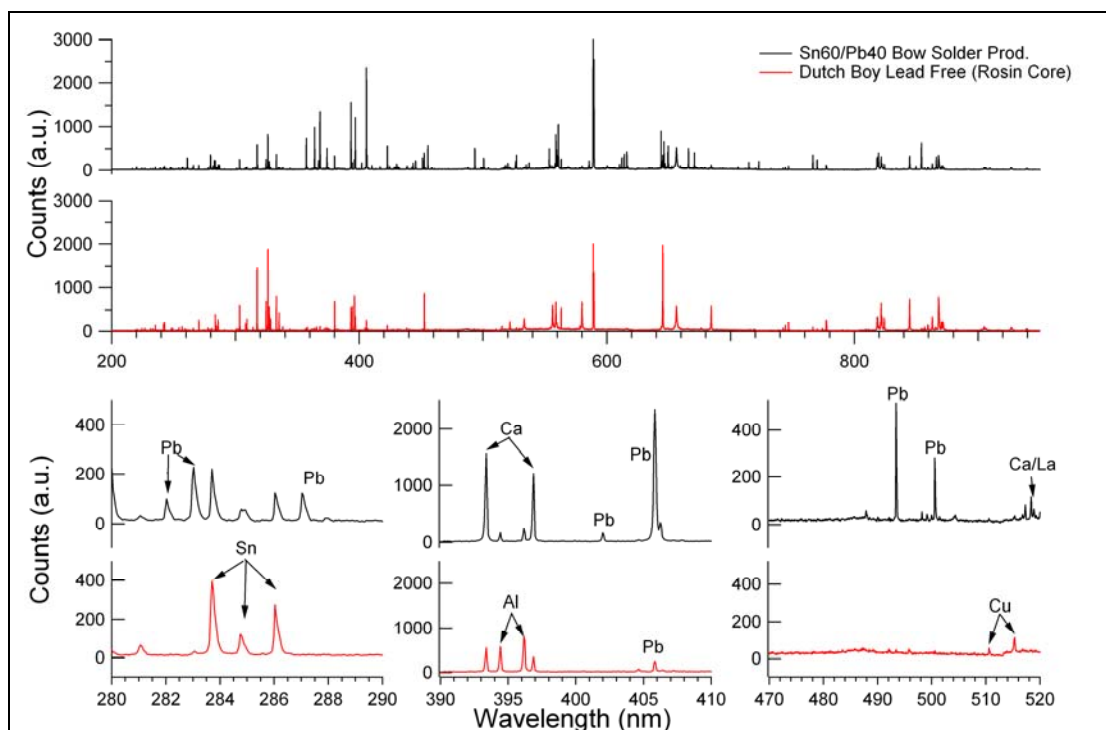


Figure 6. Single-pulse LIBS spectral comparison of Pb-containing and Pb-free solders.

Table 2. Summary of results from the chemometric analysis of solder materials.

Test Solder (# test spectra)	Correct ID Solder Type (%)	False Positive (%)	Correct ID (%) Pb/Pb-Free	False Positive (%) Pb/Pb-free
2.2 mm dia. Pb-based (6)	100	8.5	100	0.0
1.1 mm dia. Pb-based (6)	83.3	1.2	100	0.0
Sn60/Pb40 Bow Solder (19)	100	0.0	100	0.0
0.32" Silver-bearing (20)	100	0.0	100	0.0
Dutch Boy Lead-Free, Rosin core (16)	87.5	2.4	100	0.0
Dutch Boy Lead-Free, Acid core (9)	100	2.4	100	0.0
Dutch Boy, Lead-Free, no core (6)	100	2.4	100	0.0

Another example application is a recent study characterizing steel samples (67). Figure 7 shows several spectral regions of LIBS spectra from three steel alloys. The need to analyze steel samples for their chemical composition is important for process control. Most methods currently employed generally require sample preparation steps and off-site analysis. Benet Laboratories (U.S. Army ARDEC) wanted to determine slight discrepancies in the composition of steel parts. Benet provided several steel samples to ARL, and a laboratory bench-top LIBS system was used to confirm that the steel samples provided were 4130 steel standards. Based on the linear correlation of the steel sample spectra with a spectral library, we were able to confirm the composition of the Benet samples.

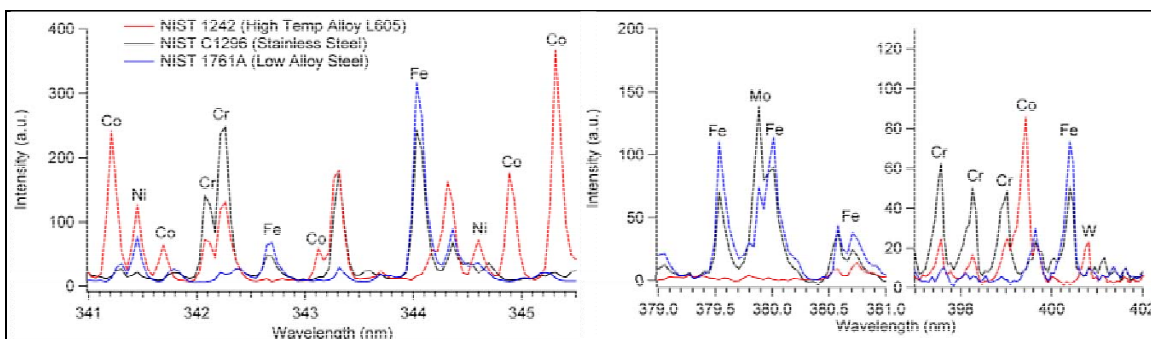


Figure 7. Single-pulse LIBS spectra of three NIST-certified standard reference steel alloys. Observed minor constituents include Co, Cr, W, Ni, and Mo.

One interesting application of LIBS that has not been thoroughly studied is the relationship between emission intensities and material hardness. According to Tsuyuki et al. (68), the speed of the shock front generated during plasma formation depends on the material hardness. Thus, the extent of ionization caused by the shock wave can be related to the material hardness. Tsuyuki et al. compared the compressive strength of concrete samples (including cement powders on surfaces of different hardness) to the ratio of the intensities of an ionized calcium atomic emission line, Ca II (396.8 nm) and a calcium atomic emission line, Ca I (422.6 nm). Similarly, Abdel-Salam et al. (69) demonstrated the correlation between ionized/ atomic emission ratios, Ca II (373.69 nm)/Ca I (428.9 nm) and Mg II (280.26 nm)/Mg I (285.22 nm), and the hardness of calcified tissue samples. Recently, ARL investigated the correlation between the hardness of a substrate and the ability to discriminate explosive residues on that substrate (41).

3.3 Surface Cleaning/Depth Profiling

Laser ablation has been used as a method for surface cleaning and restoration (16, 70–72). Unlike conventional methods, laser-based cleaning techniques do not rely on the use of mechanical (abrasive methods, jet spraying, etc.) or chemical solvents that can lead to inadvertent damage to the substrate (70). Advantages of laser-based cleaning methods include the ability to automate, selectivity, versatility, and a high degree of precision. The precise laser

processing parameters must be carefully optimized for each application. With LIBS, the removal of small amounts of degraded or contaminated material from the surface of a substrate is combined with the simultaneous detection of the surface composition. Therefore, the composition of each layer of material removed can be identified (depth profiling) and the complete removal of contamination signified (surface cleaning). In addition to the restoration of artwork and cultural heritage items, laser ablation has been used for the removal of unwanted coatings from a substrate (e.g., the removal of polymeric coatings from a metallic substrate). Figure 8 shows the paint layer on a car panel from a 1985 red Toyota pickup and the bare metal (titanium alloy) underneath the paint, which was revealed by sequential laser pulses. Besides depth profiling (73), other applications include surface texturing (74) and surface coating (75).

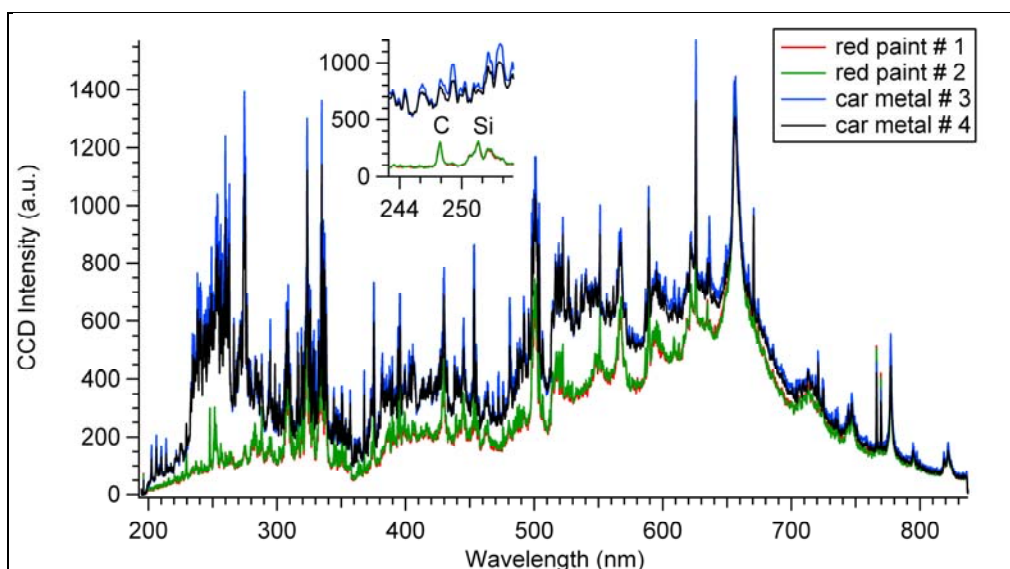


Figure 8. Standoff LIBS spectra of a car panel from a 1985 red Toyota pickup. The red paint layer and bare metal were analyzed by sequential laser pulses. The inset shows the C and Si emission lines present only in the paint.

3.4 Origin Determination

The LIBS spectra, which provide a detailed ‘fingerprint’ describing elemental composition and material properties (e.g., hardness, reflectivity, heat capacity, etc.) for each target material, can also be used to determine the origin of a sample. For example, our laboratory has used LIBS spectra (in combination with chemometric analysis) to determine provenance or locality information for various geological samples such as sea shells and soils (18), obsidians (76), and historic volcanic rocks (figure 9) (77). Counterfeiting of precious stones is a long-standing problem for the legitimate gem industry. The chemical composition of a gem, especially the concentration of trace elements, contains a chemical fingerprint of the composition of the environment in which the mineral crystallized. Because of evidence that gems are used as a source of funding for terrorist activities (27), we also investigated the use of LIBS to identify the

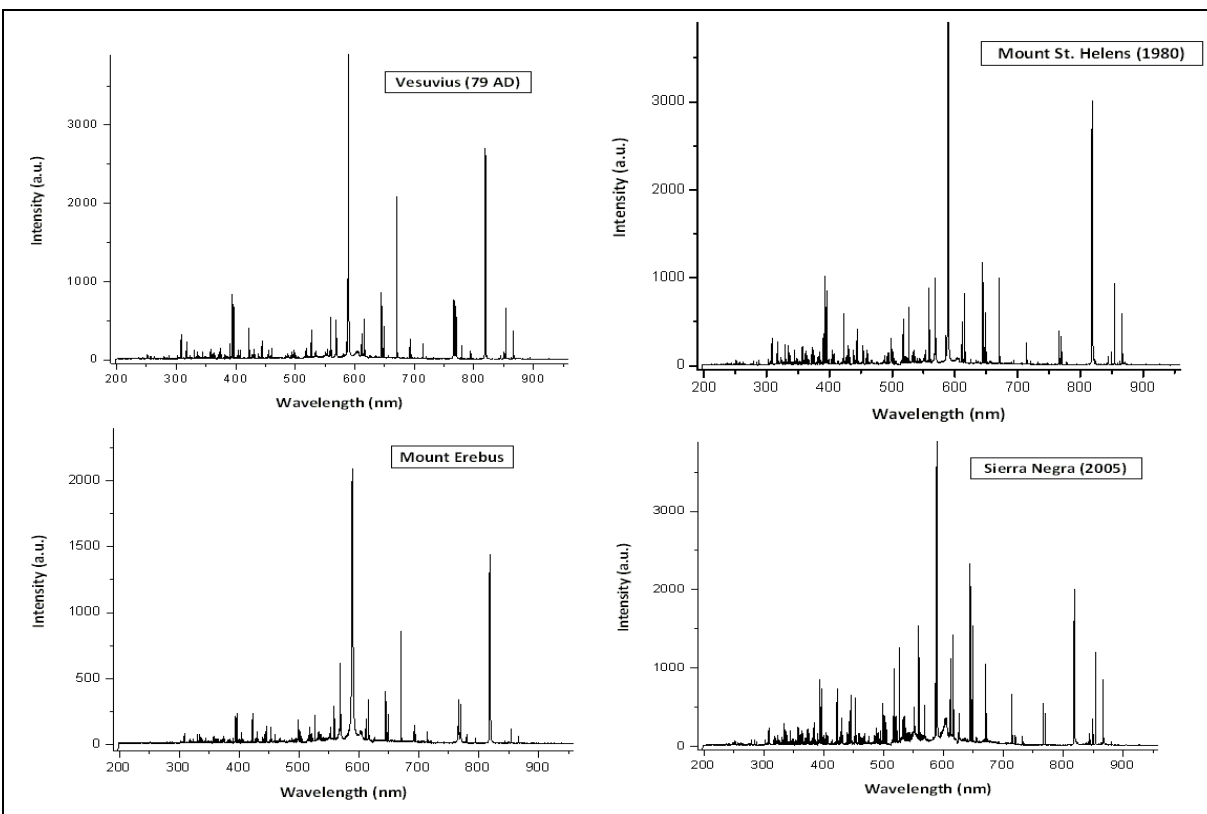


Figure 9. Representative broadband LIBS spectra of historic volcanic rocks primarily composed of SiO_2 . The source volcano and eruption period (for all 10 specimen types) were 100% identified using chemometric analysis (77).

source (geographic region, local area, or specific mine) of beryl (27, 28, 30, 31) and garnet (78) gemstones. Other promising potential applications for LIBS yet to be explored include the determination of the geographic origin of food, clothing, and other manufactured goods, as well as illicit substances such as drugs, counterfeit goods, and laundered money. It may even be possible to pinpoint specific manufacturing facilities based on trace impurities.

3.5 Compositional Mapping

Because the laser is focused tightly on the sample surface for LIBS, spatial localization is an inherent attribute of LIBS. Depending on the laser wavelength, beam divergence, beam mode quality, and focusing optics, lateral resolution on the order of $10\ \mu\text{m}$ can be obtained (73). LIBS has been used for compositional mapping, i.e., spatial mapping of the elemental composition of a sample, for a number of applications including: image mapping a copper conductor pattern from a printed circuit board (79), field analysis of inorganic wood preservatives (80), generating distribution maps of poisoning elements (phosphorous [P], Zn, and Pb) in automobile catalytic converters (81), large area mapping of non-metallic inclusions in stainless steel (82), scanning microanalysis of aluminum alloys (83), and surface mapping of granite samples (84).

Another interesting application that has not been fully explored is the detection and mapping of latent fingerprints. The detection of skin oil on a silicon wafer has been demonstrated with LIBS (85). Because trace amounts of explosive residue can be transferred from fingertips to surfaces by an individual that has previously handled explosives (86), in theory LIBS could be used to simultaneously detect the explosive residue (e.g., on a door handle) and map the structural detail of the fingerprint, enabling identification of the individual who had been handling explosive materials.

3.6 Forensics

LIBS has been applied to forensic applications, including the characterization and identification of automobile glass (87–89), the analysis of human remains and other evidence from criminal investigations (90), and the detection of gunshot powder residue (91, 92). In 2005, we performed a “proof of principle” study on the LIBS detection of mortar and rocket firing residues (93). Figure 10 shows an example LIBS spectrum from a sample coupon swiped on the outside of a mortar tube after an 82-mm mortar. Test spectra were linearly correlated against each spectrum in the library and the highest correlation coefficient (figure 10) was used to determine the identification. The red line denotes the threshold value for identifying the residue as originating from the mortar. Similar results were obtained with a residue sample acquired from the rear of a Bulgarian RPG tube post-firing. With a limited library and sample set, 100% correct matches were achieved.

3.7 Nanoparticle Production

Understanding the chemical mechanisms of combustion, thermal explosion, and detonation is essential in order to develop more efficient explosives and propellants. It is well known that two-component explosives consisting of metal particle fuels and oxidizers can produce more than twice as much energy as high performance molecular explosives alone (94). In recent years it has been suggested that nanometer-scale metal particles would provide faster energy release and better control over material properties, but the development of nanoenergetic materials has been hampered by the lack of fundamental knowledge of the chemical dynamics involved. Recently, we demonstrated the feasibility of a novel approach for studying the chemical reactions between metallic nanoparticles and molecular explosives (95). This method is based on the production of nanoparticles in a laser-induced plasma and the simultaneous observation of the LIBS emission characteristic of the species involved in the intermediate chemical reactions of the nanoenergetic material in the plasma.

Time-resolved, broadband emission of chemical species involved in the reaction of RDX and various metal nanoparticles was observed (figure 11). The increase in C_2 and AlO emission with increasing Al content previously observed during an aluminized-RDX explosion in a shock tube (96) was confirmed using this method. The time-evolution of species formation in the plasma, the effects of laser pulse energy, and the effects of trace metal content on chemical reactions were also studied. This method provides ARL with new capabilities for nanoenergetic material

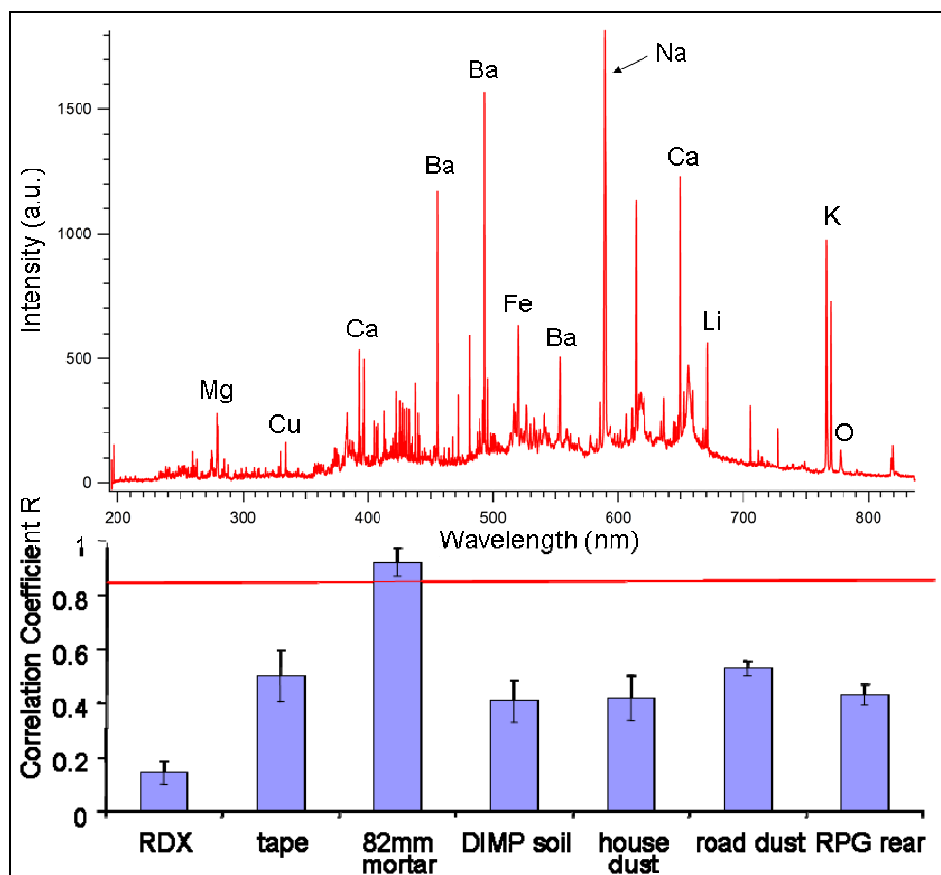


Figure 10. LIBS spectra of a sample coupon swiped on the outside of a mortar tube after an 82-mm mortar fire (top) and the linear correlation coefficients (bottom) for discrimination of the mortar residue from other sample types. The red line denotes the threshold value for identifying the residue as originating from the mortar.

evaluation and formulation, and has several advantages: (1) minimal sample preparation is required, (2) real-time, time-resolved analysis of chemical reaction intermediates can be achieved, (3) it uses small-scale, high-temperature reactions that do not require containment equipment, and (4) the ratio of fuel/oxidizer is not limited by the need to cast the explosive formulation. By monitoring the emission intensity of the different reactant species as a function of time, a better understanding of the chemistry of metallic nanoparticles and explosives at high temperatures could be achieved, eventually enabling the development of improved explosive formulations with higher explosive power and fewer harmful by-products.

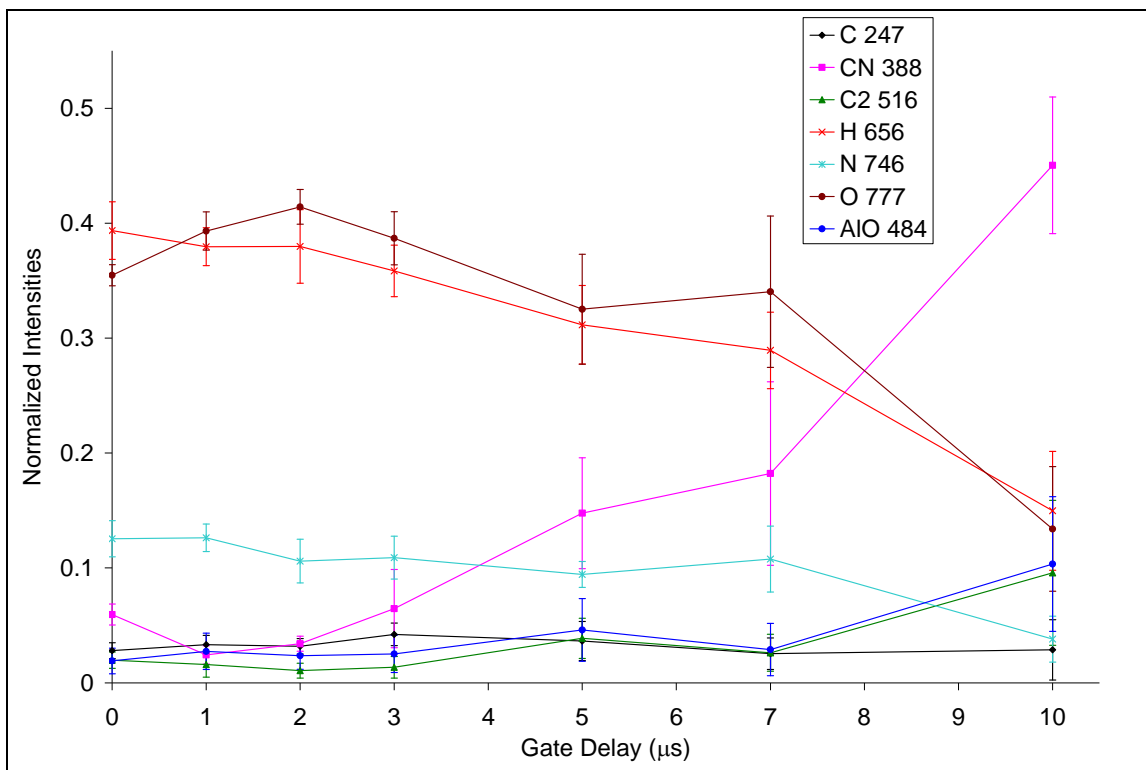


Figure 11. Emission intensities from time-resolved double-pulse spectra of RDX on Al in air at various delay times. While the concentration of atomic species slowly decreases over the first 10 μs , recombination reactions result in higher concentrations of CN, C₂, and AlO as the plasma cools.

4. Available Equipment and Software

At ARL, we have access to a variety of lasers, spectrometers, optics, optomechanics, and diagnostic equipment. We can configure laboratory LIBS setups for just about any type of sample/application. The primary laser type we use is a Nd:YAG laser (manufacturers include Big Sky Laser, Quantel USA, and Continuum, Inc.). Our Nd:YAG lasers provide nanosecond pulses at 1064 nm (or at 532, 355, or 266 nm with the proper doubling crystals and the more eye-safe 1.57 μm with the appropriate conversion module). The pulse energy can range from as little as 1 mJ to 2 J depending on laser size and wavelength. We have a wide range of spectrometers that include Czerny-Turner designs and echelle-type spectrographs from Ocean Optics, Inc., Avantes, Andor Technology, Catalina Scientific, and others. Available detectors include charge coupled devices (CCDs), intensified CCDs (ICCDs), and electron multiplying CCDs (EMCCDs). In addition to Nd:YAG lasers, we also have a femtosecond Ti-Sapphire system (Coherent Hydra) with laser pulse widths <120 fs (pulse energies up to 25 mJ) and an Optical

Parametric Oscillator (OPO) laser system (Continuum Sunlite) which provides tunable (240–1700 nm) nanosecond laser pulses. Commercially available LIBS systems in our lab include products from Ocean Optics, Inc. and Applied Photonics, Ltd., as well as a microwave-enhanced LIBS system (laser assisted microwave plasma spectroscopy, LAMPS) from Photon Machines, Inc. We also have two prototype standoff LIBS instruments that can collect spectra ranging from 10 to 100 m.

For sample preparation, we have a commercial inkjet-based printing platform (Microfab Jetlab4). This system enables quantitative sample deposition on a variety of surfaces and complex print job definition through scripting. It is currently being used to determine limits of detection for explosive residues using LIBS.

With funding from ARL, Signal Innovations Group has recently developed software to automate the chemometric analysis of LIBS data with algorithms developed at ARL. This software has provided ARL with the capability for real-time identification of materials based on LIBS. A video demonstration of the identification of biological powders using the automation software and ARL-developed algorithms is available on our website at <http://www.arl.army.mil/www/default.cfm?Action=247&Page=462>. The software can be adapted to work with any LIBS system for any application.

5. Conclusions

While the primary focus of LIBS at ARL has been hazardous material detection, LIBS has a number of other applications that could benefit the U.S. Army. Since the broadband spectrometers observe every element on the periodic table, the composition of any material can be determined. Broadband LIBS spectra coupled with advanced chemometric analysis can provide a wealth of information about a particular sample. While the applications are seemingly limitless, the best applications will utilize the strengths of LIBS, e.g., speed of analysis, flexibility of experimental design, and lack of sample preparation.

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